

U.S. Serial No. 09/811,248
Amendment dated October 16, 2008

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Amendments to the Specification:

Please add the following new paragraphs after the heading

"Detailed Description of the Invention":

[0001] The hydrogel foams produced in accordance with the present invention have properties that make them uniquely adapted for use as superabsorbent materials. One unique property of hydrogel foams is their ability to swell extremely fast in aqueous solution. When the dried hydrogel foam of the present invention (having an open cell structure) is placed in an aqueous solution, water flows through the open channels by capillary effect, and rapidly swells the hydrogels. Conventional hydrogels also swell upon contact with an aqueous solution, but the swelling rate is much slower. For example, when hydrogels and hydrogel foams are formed in the size of conventional tablets (having a size range of 5-10 mm in diameter) and are contacted with water, hydrogel foams will complete swelling in less than an hour, while the hydrogels take more than 12 hours to reach an equilibrium swelling.

[0002] Hydrogel foams also swell to a much larger extent than the conventional hydrogels made of the same materials at the same concentration. Hydrogel foams in accordance with this invention can absorb more than 100 times its own weight of aqueous solution. In one embodiment in accordance with the present invention, a hydrogel foam is formed wherein the ratio of the volume of the gas phase to the volume of the solid phase is at least one. In another embodiment, a volume of the hydrogel foam of this invention having a size greater than 1 mm in its smallest dimension exhibits a water swelling ratio of at least 15 within one hour of contact with an aqueous solution. In a further embodiment, a volume of the hydrogel foam of this invention having a size greater than 1 mm in its smallest dimension exhibits at least 50% of its maximum swelling ratio within one hour of contact with an aqueous solution.

[0003] The hydrogel foams of the present invention are prepared by introducing a gas into an monomer solution comprising at least one hydrophilic olefin monomer compound, about 0.1 to about 10% by weight of a multiolefin-functional crosslinking agent and a surfactant, during polymerization of the olefin monomer. Preferably the polymerization reaction is conducted in an aqueous solution; however non-aqueous solvents, preferably water miscible non-aqueous solvents such as alcohols, ethers, dimethyl sulfide, dimethyl formamide and the like, can also be used to form the hydrogel foams in accordance with the present invention.

[0004] Hydrophilic olefin monomers for use in accordance with the present invention include those monomers having hydroxyl, keto and amino functionalities in addition to the alkene functionality. Suitable hydrophilic monomers for synthesizing hydrogels are known to those skilled in the art and include the hydrophilic monomers/polymers described in U.S. Pat. Nos. 4,178,361 and 3,551,556, the disclosure of which is expressly incorporated herein by reference. In particular, hydrogel foams of poly(acrylic acid) (PAA), polyacrylamide (PAM), polyvinylpyrrolidone (PVP), poly(2-hydroxyethyl methacrylate) (PEMA), and poly(2-hydroxypropyl methacrylate) (PHPMA) have been prepared.

U.S. Serial No. 09/811,248
Amendment dated October 16, 2008

[0005] Some suitable examples of hydrophilic monomers include hydroxy lower alkyl acrylates or methacrylates, or hydroxy lower alkoxy lower alkyl acrylates or methacrylates such as 2-hydroxy ethyl acrylate, 2-hydroxy ethyl methacrylate, diethylene glycol monoacrylate, diethylene glycol monomethacrylate, 2-hydroxy propyl acrylate, 2-hydroxy propyl methacrylate, 3-hydroxy propyl acrylate, 3-hydroxy propyl methacrylate, and dipropylene glycol monomethacrylate. Other suitable hydrophilic monomers include the heterocyclic polymerizable compounds containing a carbonyl functionality adjacent to the nitrogen in the heterocyclic ring such as the N-vinyl lactams, N-vinyl imidazolidones, N-vinyl succinimide, N-vinyl diglycolylimide, N-vinyl glutarimide, N-vinyl-3-morpholinone, N-vinyl-5-methyl-3-morpholinone. Usually the heterocyclic compounds contain from about 3 to 6 carbon atoms in the ring. Examples of some contemplated N-vinyl lactams include N-vinyl-2-pyrrolidone, N-vinyl-2-piperidone, and N-vinyl-ε-caprolactam.

[0006] It is also anticipated that the hydrogel foams of the present invention can be formed from solutions of several different monomer species to form a co-polymer based hydrogel foam. The concentration of the monomer ranges from 5% to 80% depending on the type of the monomer. The minimum concentration of monomer in aqueous reaction mixtures required to form a foam structure that maintains its structural integrity has been determined for the following monomers:

Acrylamide	5%
Acrylic Acid	8%
Vinylpyrrolidone	15%
2-Hydroxyethyl methacrylate	40%
2-Hydroxypropyl methacrylate	80%

[0007] Polymerization of the olefin monomers is initiated by a free radical mediated reaction. Free radical initiators are well known in the art and the nature of such is not typically critical to the polymerization reaction. Ammonium persulfate (APS) and N, N, N', N'-tetramethylethyldiamine (TEMED) have been used as the initiators for PAM, PAA, PIIPMA and PHEMA hydrogels, while 2, 2'-azobis (2-amidinopropane) dihydrochloride (Wako Pure Chemicals), a water soluble azo-initiator has been used for PVP and gels.

[0008] The olefin monomers are polymerized in the presence of a multiolefin-functional crosslinking agent. Typically the crosslinking agent concentration ranges from about 0.1 to about 10%, more typically about 0.1 to about 1.5% by weight relative to the olefin monomer. A multiolefin-functional crosslinking agent is defined herein to include any compound having at least two alkenyl groups. One multiolefin-functional crosslinking agent used in accordance with the present invention is N, N'-methylene-bis-acrylamide (BIS). Other suitable bifunctional olefin crosslinking agents include diallyl phthalate, diallyl isophthalate, diallyl benzene and divinyl pyridine. The crosslinking agent can also be a biodegradable protein or carbohydrate that has been functionalized by covalent coupling with compounds bearing pendent alkenyl groups.

[0009] The hydrogel foams of the present invention are formed by introducing gas into a hydrophilic olefin monomer solution during polymerization of the monomer. The gas can be introduced into the polymerizing matrix by mechanical means or through the use of a blowing agent (or foaming agent). Mechanical means includes the use of a high speed blender or propeller

U.S. Serial No. 09/811,248
Amendment dated October 16, 2008

or the introduction of gas into the liquid through a capillary or microporous surface. A blowing agent is defined herein as any substance or combination of substances capable of producing a gas upon exposure to environmental or chemical reagents. Examples of blowing agents are carbonates or metal powders which react with acidic condensation catalysts to generate CO₂ or H₂ and chemical agents that liberate expanding gas under the influence of heat, such as dipotassium-diazomethionate, N-nitroso- β -amino ketones and sodium borohydride. Combinations of various blowing agents or combinations of blowing agents with mechanical means can also be used to introduce gas into the hydrophilic olefin monomer solution during polymerization of the monomer.

[0010] In one embodiment the hydrogel foam includes one or more functional particulate fillers. Appropriate fillers for use in accordance with the present invention include materials that increase the strength of the foam or highly absorbent materials, such as activated charcoal or other carbon materials that augment the absorption characteristics of the foam. Preferably the added fillers are evenly dispersed throughout the monomer solution during the polymerization reaction. This can be accomplished through the use of mixing, for example the use of a high speed mixer or blender. The concentration of the added filler is limited to levels which do not interfere with foam functionality.

[0011] In one embodiment about 1% (by weight) of carbon particles was added to the monomer solution to form a hydrogel foam. It is anticipated that carbon particles can be added up to a concentration of about 10% without effecting the formation of the foam.

Please add the following new paragraphs after Example 16:

[0012] EXAMPLE 17

[0013] Synthesis of Poly(acrylic Acid) Foams

[0014] Poly(acrylic acid) foams have been prepared using either N, N'-methylene-bis-acrylamide (BIS) or functionalized albumin as a crosslinking agent. In polyacrylic acid foams crosslinked with BIS, the BIS was dissolved in acrylic acid (AA) to make a final concentration of 1% (w/v) BIS (i.e., 150 mg of BIS was dissolved in 15 ml of AA). All the components were then mixed in a glass test tube (15x85 mm) containing deionized distilled water (DDW) as described in Table 1.

TABLE 1

	Amounts of each components added to make <u>poly(acrylic acid) hydrogel foams.</u>		
	<u>Foam 1</u>	<u>Foam 2</u>	<u>Foam 3</u>
AA/BIS mixture	0.2 ml	0.3 ml	0.4 ml
DDW	0.6 ml	0.5 ml	0.3 ml
TEMED (10%)	50 μ l	50 μ l	50 μ l
NaHCO ₃	0.1 ml	0.1 ml	0.2 ml
APS (10%)	50 μ l	50 μ l	50 μ l

[0015] Ammonium persulfate (APS) was added last. After the addition of APS, the tube was immediately immersed in a 60°C water bath about 15 sec. After the test tube was removed from

U.S. Serial No. 09/811,248
Amendment dated October 16, 2008

the water bath, a NaHCO_3 suspension (70% w/v) was added dropwise every 5-10 sec with constant shaking by hand. In the beginning, foaming was vigorous due to the strong acidic pH. Addition of NaHCO_3 raised the pII of the solution towards a neutral pH which is more favorable for redox initiation. As the amount of the added NaHCO_3 increased (about 2-3 drops) the pH of the mixture became high enough for the initiators to start the polymerization reaction. The optimum pH for TEMED-APS initiators is between 8 and 9. However such a high pH is not desirable, since acidic pH is necessary for the decomposition of NaHCO_3 .

[0016] PAA is partially neutralized by NaHCO_3 during foaming. This built-in neutralization effect results in extremely fast swelling of the PAA hydrogel foams even in the absence of the surfactant albumin during synthesis of the foam. The swelling ratio during the first 5 min of hydration was larger than 10. The PAA hydrogel foam reached 70% of the equilibrium swelling within 30 min, while conventional PAA hydrogel took more than 3 days to reach 70% of the equilibrium swelling.